APPLICATION OF NON-AQUEOUS SOLVENTS TO BATTERIES

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Introduction

Since the OPEC crisis of the 1970s, there has been a general realization of the fact that we need to conserve the existing fossilized fuel and maximise the use of alternative sources of renewable energy such as solar energy. The key to achieving this lies in the development of suitable energy storage systems. It is generally accepted that rechargeable electrochemical batteries offer the most flexible and versatile means of storing energy. Batteries are needed for electric vehicle propulsion, electric utility load-levelling, and bulk energy storage application. The lead/acid battery is currently used for all these applications, but its performance is inadequate for most applications. Low power to weight ratio and poor cycle life are the major problems, and it is generally believed that development of more suitable advanced batteries is essential to meet the future energy demands.

Since the mid-1970s extensive worldwide effort has been directed towards battery research and development. A number of reviews could be referred to on this subject [1 - 4]. Unfortunately, in spite of the advances made, so far none of the new concept batteries has reached a commercialization level. Thus, the search for advanced batteries must continue.

Looking back at the research activity on batteries, it is quite obvious that the application of non-aqueous or aquo-organic solvents to batteries has attracted the attention of only a few researchers. Batteries based on aqueous electrolytes or molten salts have been more actively investigated, and the use of organic solvents has been considered only for batteries which use alkali metals, due to the reactivity of these metals with aqueous electrolytes.

Parker and co-workers [5 - 7] have demonstrated the usefulness of solvents, other than water, to minerals and energy industries. Compared with water, non-aqueous solvents offer different anion and cation solvating properties, different solvation of uncharged solutes, and different reaction rates. They offer a wide range of temperatures for their liquid states, viscosities, ionic mobilities, ionic conductance, and redox stability [8]. Suitable solvent properties are of extreme importance in the development of batteries. Since organic solvents offer a wide range of such properties, their use in battery development is very relevant. The following sections discuss some

of the examples where organic or aquo-organic solvents have been successfully used by us, and also note other areas of battery technology where their use could be most appropriate.

Application to lithium batteries

Organic solvents offer the convenience of obtaining desirable solution properties simply by mixing two or more of the solvents with appropriate characteristics. For example, propylene carbonate (PC) is often used as a solvent for lithium batteries. This solvent has all the desirable characteristics for this application, *i.e.*, it has a high dielectric constant, high electrolyte solubility and, more importantly, is stable towards lithium except that it is very viscous (2.53 cP). The high viscosity results in low electrolyte conductivities and therefore lithium batteries suffer from high ohmic losses. The solution conductivity is significantly improved by mixing PC with low viscosity solvents such as tetrahydrofuran (THF) [9] or dimethoxyethane (DME) [10]. The ethers on their own are not particularly suitable for lithium battery application because they have low dielectric constants and low electrolyte solubilities and, hence, electrolyte solutions in these solvents are very poorly conducting.

We have achieved high electrolyte solution conductivities by mixing PC with acetonitrile (AN). Acetonitrile has a low viscosity (0.35 cP) and a moderately high dielectric constant (37). Thus mixtures of PC and AN ensure good electrolyte conductance. Unfortunately, acetonitrile reacts with lithium and therefore, under normal circumstances, PC/AN mixtures are unsuitable for battery applications. However, we have found that lithium is quite stable in 50% v/v AN/PC mixtures in the presence of $LiAsF_6$ electrolyte [11]; presumably a protective film involving AsF_6^- is responsible for this effect. The use of 1M $LiAsF_6$ in 50% PC/AN offers several advantages over 1M $LiAsF_6$ in PC for lithium batteries which use certain intercalation compounds as cathodes, as is shown in Table 1. Higher cathode utilization and energy efficiencies are achieved in PC/AN than in PC. This observation is related to smaller IR effects and the differences in the ease of intercalation of the solvated lithium ions. The solvation energies of lithium in PC and AN are quite different ($\Delta G_t Li^+$ from PC to AN + 6 kJ mol^{-1}) and the molar volumes of the solvated ions in PC and PC/AN could vary depending on the solvation shell composition. Thus, the behaviour of intercalation cathodes is quite different in PC and in PC/AN.

Application to zinc bromine battery

Organic reagents have found useful application in the development of circulating-electrolyte zinc/bromine batteries currently being developed by Exxon [12] and Gould [13] laboratories in the U.S.A. The historic problem

TABLE 1

Comparison of PC and 50% PC/AN for lithium intercalation cells at 25 °C 1M LiAsF$_6$ as electrolyte, discharge at 2 mA cm^{-2}

Cathode	PC			50% PC/AN		
	W h kg^{-1} cathode	Utilis.[f] (%)	Energy[g] effic. (%)	W h kg^{-1} [d] cathode	Utilis.[f] (%)	Energy effic. (%)
V$_2$O$_5$[b]	230	63(1)	49	310	81	63
V$_6$O$_{13}$[a,e]	370	43(8)	28	700	63	52
MoO$_3$[a]	110	15(2)	11	560	76	54
MnO$_2$[a]	430	36(2)	20	>600	>40	>35
Cu$_2$S[c]	190	39(2)	24	350	66	45

[a]Cut off voltage is 1.6 V.
[b]Cut off voltage is 2 V.
[c]Cut off voltage is 1.3 V.
[d]Observed energy density to cut off voltage based only on weight of active cathodic material.
[e]Discharged at 1 mA cm^{-2}.
[f]Utilisation of cathode to cut off voltage based on intercalation of the number of Li moles shown per mole of cathode material.
[g]Energy efficiency is the observed energy density as a percentage of the theoretical energy density.

of self-discharge of the zinc/bromine battery has hindered its development so far in spite of its attractive energy density and other electrochemical characteristics. The Exxon and Gould research groups have successfully overcome this problem by using a two-phase electrolyte in which bromine is complexed with tetraalkyl-ammonium salts into a water immiscible oil.

We have found that we can overcome the self-discharge problem even more simply by dissolving bromine and bromide salt in water immiscible, dipolar aprotic solvent—proprionitrile (PN) [14]. The nitrile is stable in battery environments, forms a charge-transfer complex [15] with bromine, and results in a two-phase system with water in which the distribution coefficient of bromine is ca. 50. The nitrile, like many other organic solvents, strongly favours the formation of Br$_3^-$ ions via the equilibrium Br$_2$ + Br$^-$ ⇌ Br$_3^-$. The equilibrium constants of this reaction in some organic solvents are recorded in Table 2. The higher solvating ability of organic solvents for Br$_2$ and Br$_3^-$ as compared with water is responsible for this result. Due to the formation of Br$_3^-$ and the PN–Br$_2$ charge transfer complex, the solutions containing bromine and bromide salts are highly conducting. We have shown that the zinc/bromine cells which use this PN/H$_2$O two-phase system have high energy efficiency (>75%) and high coulombic efficiency (>85%) [16]. Further, the battery has less problems with zinc dendrite formation during cycling, which is an acute problem in alkaline–zinc batteries. The battery in this form is most suitable for electric

TABLE 2

Molar-scale equilibrium constants (K_c) for the reaction
$Br_2 + Br^- \rightleftharpoons Br_3^-$ in various solvents at 25 °C[a]

Solvent	K_c (l mole^{-1})
Water	16.4
Methanol	177
Acetic acid	150
Nitromethane[b]	$10^{7.2}$
Sulfolene[c]	$10^{6.8}$
Acetone	2×10^9
Dimethylformamide[b]	2×10^6
Acetonitrile[b]	10^7
Propionitrile[d]	10^7

[a]Data quoted from A. J. Bard (ed.), *Encyclopedia of Electrochemistry of Elements*, Vol. 1, Dekker, New York, 1973.
[b]At 20 °C.
[c]At 22 °C.
[d]P. Singh and S. Jayasekera, unpublished work.

vehicle, utility load levelling, and bulk energy storage applications and compares favourably with Exxon and Gould concepts [16].

Possible future applications

Redox batteries have received considerable attention recently, particularly by NASA which is developing a battery based on Cr^{3+}/Cr^{2+} and Fe^{3+}/Fe^{2+} couples in acidic–aqueous solutions [17]. The battery consists of two inert electrodes separated by a suitable separator. The electrolytes are stored outside the battery in two separate reservoirs and are circulated through the cell only when required. This concept is very attractive for solar energy or any other form of bulk energy storage. The cell reaction is as follows:

$$Cr^{2+} + Fe^{3+} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Cr^{3+} + Fe^{2+}$$
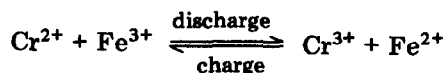
cell potential = 1.2 V

Since this battery concept does not use any solid electroactive material, the usual problems of dendrite formation, electroactive material shedding, electrode slumping, etc., are absent. The cycle life of the cell is limited only by the chemical stability of the electrolyte solution.

Figure 1 shows that Cr^{2+} is thermodynamically unstable in aqueous solution and reacts with water producing hydrogen gas, hence provisions
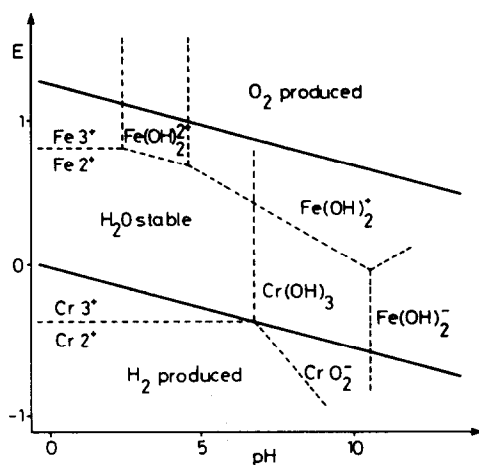
Fig. 1. Eh–pH diagram of the Fe–H_2O and Cr–H_2O systems.

have to be made to overcome the solvent stability problem. This adds unnecessary complications to the battery design. The problem could probably be solved by choosing couples which are stable in aqueous environment, but this would lead to lower cell voltage.

Redox batteries based on couples such as $VO^{2+}/VO_2^+-Sn^{4+}/Sn^{2+}$; $VO^{2+}/VO_2^+-Fe^{3+}/Fe^{2+}$ and $VO^{2+}/VO_2^+-Cu^{2+}/Cu$ in aqueous solutions have also been considered for redox battery application [18]. However, slow electron transfers are inherent problems associated with these systems.

Redox battery development is an area where organic solvents can hopefully play an important role. Due to the well-known ion–solvent interactions, the organic solvents influence the electrode potentials of redox couples and this effect could be exploited to produce redox batteries with
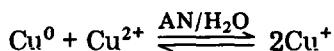
TABLE 3

E^0 Cu^+/Cu^0 at E^0 Cu^{2+}/Cu^+ in acetonitrile/water (AN/H_2O) mixtures vs. standard hydrogen electrode[a] (25 °C)

Solvent composition (mole % AN in AN/H_2O)	E^0 Cu^+/Cu^0 (V)	E^0 Cu^{2+}/Cu^+ (V)
0	0.524[b]	0.158[b]
5.7	0.236	0.520
12.7	0.158	0.620
25.4	0.118	0.672
65.9	0.025	0.800
100	0.026	1.226

[a]Data from P. Singh, *Ph.D. Thesis*, Murdoch University, Western Australia, 1980.
[b]M. Pourbaix, *Atlas of Electrochemical Equilibrium in Aqueous Solutions*, Pergamon Press, Oxford, 1966.

quite high cell voltages. A good example is that of the influence of AN on Cu^{2+}/Cu^+ and Cu^+/Cu^0 couples. Table 3 shows that as the concentration of AN in H_2O is increased, the E^0 Cu^+/Cu^0 tends to become more cathodic whereas the E^0 Cu^{2+}/Cu^+ becomes more anodic. Thus, in the presence of AN in AN/H_2O solvent mixtures, Cu^0 can react with Cu^{2+} as follows:

$$Cu^0 + Cu^{2+} \xrightleftharpoons{AN/H_2O} 2Cu^+$$

One could utilize this redox reaction to construct a battery whose open-circuit voltage will depend on the concentration of AN in the solvent mixture and can be theoretically calculated from the data in Table 3. We have

TABLE 4

Oxidation half-wave potentials ($E_{1/2}$) for some complexes of iron, ruthenium, osmium, cobalt and chromium[a]

Complex	DMF	AN	aq
	a/V	a/V	a/V
$Fe(bipy)_3^{2+}$	+1.06	+1.03	+0.81
$Fe(4\text{-}dmbipy)_3^{2+}$	+0.92	+0.87	+0.65
$Fe(5\text{-}dmbipy)_3^{2+}$	+0.96	+0.92	+0.73
$Ru(bipy)_3^{2+}$	—	+1.20	—
$Ru(4\text{-}dmbipy)_3^{2+}$	—	+1.09	—
$Ru(5\text{-}dmbipy)_3^{2+}$	—	+1.13	—
$Os(bipy)_3^{2+}$	+0.83	+0.81	—
$Os(4\text{-}dmbipy)_3^{2+}$	+0.71	+0.65	—
$Os(5\text{-}dmbipy)_3^{2+}$	+0.76	+0.70	—
$Co(bipy)_3^{2+}$	+0.31	+0.28	—
$Co(4\text{-}dmbipy)_3^{2+}$	+0.21	+0.15	—
$Co(5\text{-}dmbipy)_3^{2+}$	+0.26	+0.19	—
$Co(bipy)_3^{+}$	−0.88	−0.97	—
$Co(4\text{-}dmbipy)_3^{+}$	−1.02	−1.12	—
$Co(5\text{-}dmbipy)_3^{+}$	−0.97	−1.07	—
$Cr(bipy)_3^{2+}$	−0.23	−0.26	−0.47
$Cr(4\text{-}dmbipy)_3^{2+}$	−0.37	−0.42	−0.66
$Cr(5\text{-}dmbipy)_3^{2+}$	−0.32	−0.36	−0.54
$Cr(bipy)_3^{+}$	−0.69	−0.76	—
$Cr(4\text{-}dmbipy)_3^{+}$	−0.82	−0.91	—
$Cr(5\text{-}dmbipy)_3^{+}$	−0.79	−0.87	—
$Cr(bipy)_3$	−1.21	−1.32	—
$Cr(4\text{-}dmbipy)_3$	−1.34	−1.42	—
$Cr(5\text{-}dmbipy)_3$	−1.37	−1.48	—
$Cr(bipy)_3^{-}$	−1.87	−1.94	—
$Cr(4\text{-}dmbipy)_3^{-}$	−1.94	−2.00	—
$Cr(5\text{-}dmbipy)_3^{-}$	−2.01	−2.08	—
$Fe(bipy)_3^{+}/Fe(bipy)_3^{2+}$	−1.26[b]	—	—
$Cr(bipy)_3^{+}/Cr(bipy)_3^{2+}$	−0.72[b]	—	—

[a]Data quoted from T. Saji and S. Aoyagui, *J. Electroanal. Chem.*, 60 (1975) 1.
[b]T. Saji and S. Aoyagui, *J. Electroanal. Chem.*, 63 (1975) 405.

investigated this battery in detail and the results of our findings will be published at a later date. An economic analysis of this battery concept as an extension to the Parker Copper Refining Process [7] has been considered by AMDEL [19]. A battery based on the copper couples in pure AN has been demonstrated by Kratochvil [20].

There are numerous other redox couples which, in fact, could be used in solution form and result in redox batteries with high open-circuit voltages [21 - 24]. Table 4 lists some representative redox couples. As expected, the $E_{1/2}$ values for these couples are quite different in water and organic solvents. Solubilities and stabilities of such couples in polar organic solvents are usually higher than in water. Thus, it is more appropriate to use organic solvents for their application to redox flow batteries. The electron transfer kinetics of some of these couples are known to be fast [25 - 27] and thus high current densities are possible. A proper evaluation of their usefulness is necessary.

Conclusion

The examples considered in this paper suggest that interesting new battery concepts could emerge if more attention was directed towards the application of non-aqueous solvents to battery research. The field is wide open and it is hoped that this area of research will gain momentum in the future.

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